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SORPTION OF WATER IN MORTARS AND CONCRETE

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Abstract

Results are presented of a study on the capillary transport of water in concretes and mortars as a function of water/cement ratio, sand size distribution, and curing. Our studies indicate that the sorption of water with respect to time in concrete exhibits complex scaling behavior. At early times, of the order of one hour, the $t^{1/2}$ scaling of typical sorption theories is observed. At longer times, of the order of tens of days, a slow crossover regime is seen as the $t^{1/2}$ scaling breaks down. At very long times, of order hundreds of days, a slower uptake which may be driven by the capillary forces in the smaller gel pores is found. Again a $t^{1/2}$ scaling is observed but with a much smaller sorption rate. We describe an empirical fitting form for data in the different scaling regimes. Aspects of the experimental design including sample drying and exposure to air are discussed. Service life predictions from such measurements are discussed.

Introduction

Moisture transport in porous media plays an important role in the degradation of building materials such as mortar and concrete (Hall 1994). In particular, the invasion of water in building materials provides a mechanism and path for the penetration of deleterious materials like chloride and sulfate ions. The presence of water can also lead to cracks which result from freeze/thaw cycles or, in combination with very low permeabilities, to the spalling (Hertz 1984) of high performance concrete exposed to fires. Clearly, an understanding of moisture transport in concrete and mortar is important in order to estimate their service

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life as building materials and to improve their quality.

The primary transport mechanisms by which chloride and sulfate ions ingress concrete are diffusion and capillary action. Since diffusion alone can be a very slow process, it may be that capillary transport, especially near the concrete surface, is the dominant invasion mechanism.

Tests which directly measure the rate of capillary sorption, such as the Concrete Absorption Test (CAT) (Dhir et al. 1987) and the Initial Surface Absorption Test (ISAT) (Levitt 1969) typically make measurements over a period of about an hour. Measurements over such short periods of time will only probe surface effects and cannot provide sufficient information for the modelling of capillary transport over longer periods, which is needed for service life prediction.

Capillary Transport

Sorption of water in porous media is typically described by the following equation (Hall 1994),

$$W/A = St^{1/2} + S_o \quad (1)$$

where W is the volume of water absorbed, A is the sample surface area exposed to water, S is the sorptivity and S_o is a correction term added to account for surface effects at the time the specimen is placed in contact with the water. Equation 1 is based on the assumption that the pore structure has a tube-like topology and that the meniscus, formed at the air water interface, is a spherical cap.

Of course, a random porous material like concrete cannot be accurately modeled as a collection of tubes. The pore surface topology is far more complex so that, as the air/water interface moves through the porous medium, there are many orientations of the local interface which may be stable despite the smallness of the pore size. Also, deviation from the $t^{1/2}$ scaling in equation 1, over longer time scales, may be the result of modification of the pore structure due to, for instance, leaching (Bentz and Garboczi 1992) or further hydration as the water is absorbed. For instance, while hydration will reduce the typical pore size in the cement paste matrix, slowing the sorption of water, leaching opens up pores, making them larger and more connected such that sorption could be enhanced. However, it has not been quantitatively demonstrated how such alterations of the pore structure affect a material's sorptivity. In addition, the dissolution of salts may reduce the rate of sorption (Sosoro and Reinhardt). Finally, moisture transport in concrete must depend on factors such as the degree of saturation and environmental conditions.

In this paper we present results of a study concerning capillary transport, over periods of about one year, in mortars and concrete. Variables considered were the water-to-cement ratio (W/C), sand size distribution, and amount of

curing. We discuss several issues concerning sample preparation and boundary conditions. The existence of two different scaling regimes associated with capillary sorption in mortar and concrete was found. An empirical function is suggested which accurately fits data in the different scaling regimes.

Experiment

The measurement of water sorption is, in principle, a very simple experiment. After a standard preparation method described below, mortar and concrete cylindrical specimens were exposed to a liquid on one of the plane ends by placing them in a pan as shown in Figure 1. The fluid level in the pan was

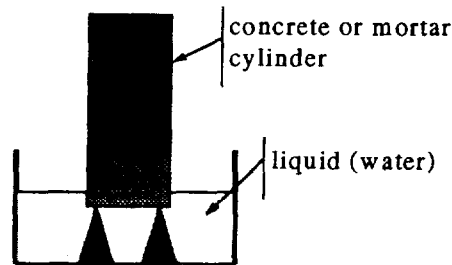


Figure 1: Experimental set-up. A mortar or concrete specimen is placed in a tray filled with water. The fluid level is kept constant. The mass of the specimen was monitored to determine the amount of liquid absorbed.

maintained at a constant height throughout the experiment. At regular intervals, the mass of the specimens were measured using a balance. The amount of fluid absorbed was then calculated and normalized by the cross-sectional area of the specimen exposed to the fluid.

Compositions of the Mortar and Concrete Mixtures

We studied sorption in two mortars: an ASTM C109 (ASTM 1994) mixture ($w/c=0.485$, $s/c=2.75$) and a second mixture (HPM) where $w/c=0.29$ and $s/c=1.4$. The maximum aggregate size for these mixtures was about 2mm. We also used two concrete mixtures to compare sorptivity in high and low porosity specimens. Mixture 1 had a $w/c=0.6$, $s/c=2.75$, and a gravel/cement mass ratio of 1.43. The air content of mixture 1 was 6%. Mixture 2 (HPC) had a lower air content of about 2%, with $w/c=0.36$, $s/c=2.02$, and a gravel/cement mass ratio of 1.12. The sand was a mixture of four sand grades. In addition, to improve workability, a high-range water reducer (0.09% by mass) was used in mix 2. The maximum aggregate size for the concrete mixtures was about 20mm. The

concrete specimen were made about 7 times wider than the maximum aggregate size in order to limit finite size effects due to aggregate size.

Sample Curing and Drying

Before the sorption measurements were made, the specimens were cured in limewater for periods of 1, 7 and 28 days at 20°C. Two methods for drying the samples were used. In the first, the samples were dried in an oven at 50°C until a constant mass was obtained, which took about 20 days. The second method was to air dry (also referred to as "bench dried") samples in a laboratory environment (at 20°C and 30% RH) for four days and then in a desiccator containing a desiccant for three days. To reduce exposure to the air samples were then taped on the sides. Figure 2 compares the sorption of water for the air dried and oven-dried mortar (Mix 1). Clearly the degree of saturation

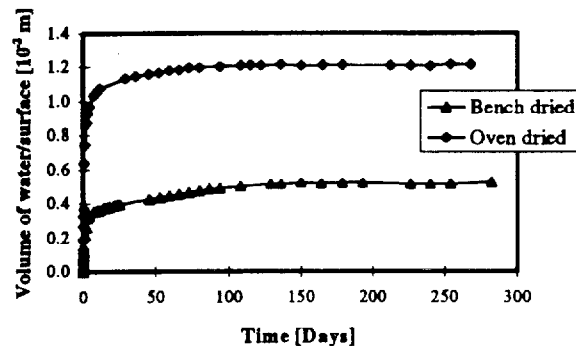


Figure 2: The influence of specimen treatment before exposure to water is shown by the rate of absorption versus time.

of the material plays a strong role in controlling the uptake of water. Over a period of about 100 days the oven-dried sample absorbed nearly three times as much water as the air-dried samples. Also fits of data to equation 1 showed that the sorptivity of the oven-dried sample was three times greater than that of the air-dried sample. It is possible that the oven drying process may have formed some cracks due to drying shrinkage resulting in greater sorption.

Figure 3 shows the sorption data for an exposure period of over 300 days for the two concrete mixtures at different curing times. We first note that

there was a moderate difference in the total water taken up for the different curing periods (about 20%). However, there was more rapid sorption in the samples that had been cured in limewater the shortest amount of time. Table 1 shows the sorptivity obtained from fits of the data in Figure 3 to equation 1. Clearly the longer the curing period the smaller the sorptivity indicating that the additional curing had reduced the pore size.

Previous studies (Hamamickova et al. 1995) have correlated other trans-

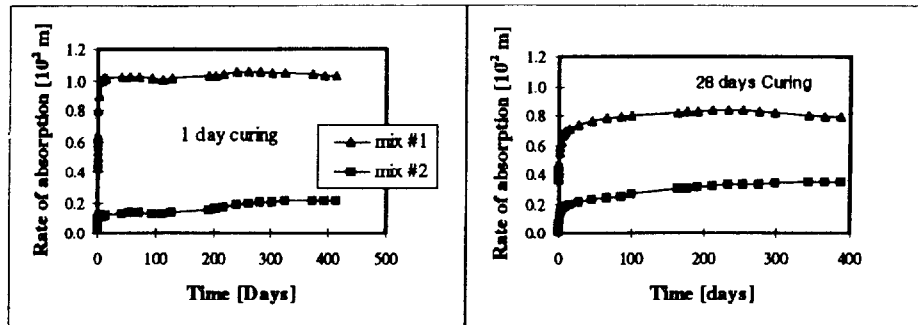


Figure 3: Comparison of water absorption for various curing periods and concrete mixture design. Mix #1: normal concrete; Mix #2: HPC. All specimens were bench dried before exposure to water.

TABLE 1
Sorptivity of Concrete Versus Time of Curing.

Concrete Mix	Sorptivity [10^{-2} m/ $\sqrt{\text{days}}$]	
	Time of curing (days)	
	1	28
#1: Conventional	0.67	0.25
#2: HPC	0.22	0.12

port properties like the diffusivity of chloride ions and permeability with curing period. For roughly equivalent curing periods it was found that the chloride diffusivity decreased by about an order of magnitude while the permeability decreased by about two orders of magnitude. Our measured sorptivities were less sensitive to the curing period, decreasing by a factor of only about 2 to 3. Scaling arguments may be used to show why permeability decreases much more rapidly with longer curing than sorption does. It has been shown that for mortars (Hamamickova et al. 1995), diffusivity scales as r_c and permeability scales as r_c^3 , where r_c is a critical pore radius based on percolation ideas (Hamamickova et al. 1995). Sorption in tube models predicts sorptivity scales as $r_c^{1/2}$ where permeability $\sim r_c^2$. Of course if permeability scales as r_c^3 (to account for tortuosity effects (Hamamickova et al. 1995)) then sorption should scale more closely with r_c . However, since the initial suction is controlled by the microstructure near the surface it is likely that tortuosity effects are less important explaining why sorption appeared less sensitive to the curing period than diffusivity.

It also appears that the sorption has nearly stopped after 200 days or so, for the conventional concrete sample. Visual examination of such samples, broken after 400 days of sorption measurements, indicated that they were not fully saturated as the water level was far from the top. However, these samples could

have been in equilibrium with the air since they were not taped on the top. Such finite size effects will be the subject of further studies. We also note that the amount of sorption can depend on mixture design. For instance, Mixture 2 was designed to produce lower porosity concrete such that less water would be absorbed.

Sorption Versus Time

Let us first consider sorption during initial exposure to water. In nearly all cases, we found that the water absorbed initially followed a $t^{1/2}$ scaling for a period of a few hours. The higher porosity mix is subject to very strong surface effects as the sorptivity data is offset from zero when $t = 0$. After a period of about 6 hours, the rate of sorption began to noticeably decrease.

Figure 4 compares sorption data for an exposure period of over 200 days for the oven dried HPM and ASTM mortars. The sorptivity data is plotted versus

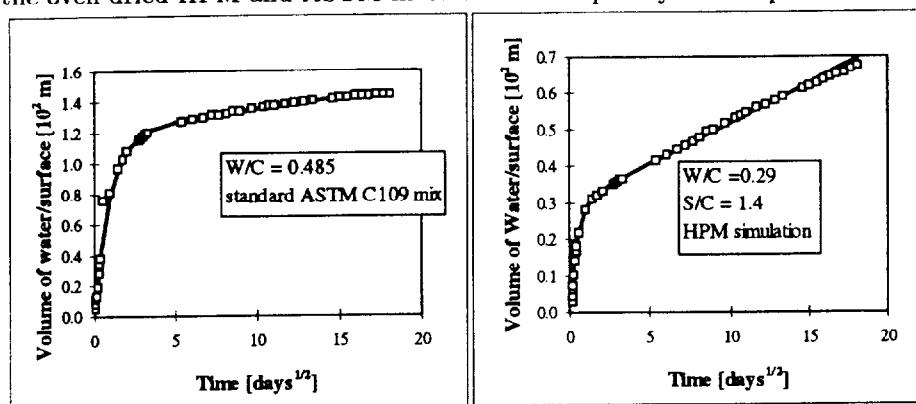


Figure 4: Sorption versus square root of days for mortars. The specimens were oven dried until constant weight, just after demolding (1 day curing).

$t^{1/2}$. Note that both the short and long time moisture sorption is consistent with $t^{1/2}$ scaling but that the sorptivity, S , (slope of the curve) is dramatically different in these regimes, differing by factors of about 30 and 80 respectively. Since $S \sim r^{1/2}$ for a straight tube model, such a difference in sorptivity would correspond to pore sizes differing by a factor of about 900 and 6400. Similarly, concrete is noted as having capillary pores of order microns and gel pores which may be several orders of magnitude smaller. Simple comparison with sorption theory would then imply that the capillary pores are dominating the sorption process at early times and that at later stages the gel pores limit the rate of flow. However, it is quite possible that, at later stages, the ingress of water may be controlled by moisture diffusion processes (Xi et al. 1994) as well.

Sorption Function

We now will focus on the issue of mathematically describing sorption as a

function of time. In nearly all cases, we found that the water absorbed followed a $t^{1/2}$ scaling over short times as described in equation 1. For periods greater than a day, there was a clear trend away from the $t^{1/2}$ scaling as the rate of sorption decreased. Gravitational effects can be ruled out, since the equilibrium height of the water would be tens of meters. Barring finite size effects, the decrease in sorption rate may be due to several factors. First, as mentioned above, as the water invades the pore space it encounters smaller pores hence slowing the rate of sorption. Second, even if the capillary pores form a strongly connected network through the specimen, such as through the interfacial zone (Bentz et al. 1995) around the aggregates where capillary pores may be larger, the ingress of water may still be slowed as the air/water interface relaxes to a stable or metastable configuration in the pore space. Then any further ingress of moisture would be controlled by capillary transport through the gel pores or moisture diffusion in the capillary and gel pores. It has been recently suggested (Sosoro and Reinhardt 1996) that as water is absorbed in concrete, calcium hydroxide is dissolved into the pore solution producing a concentration gradient which diminishes the absorption rate. Our own preliminary studies did not show a significant difference between the sorption of water or the sorption of calcium hydroxide saturated water. We are presently carrying out further studies to confirm this.

Slow relaxation phenomena and diffusion in fractal pore spaces is often described using the so-called stretched exponential function (Hubbard et al. 1992). To model the transition from rapid to slow sorption rates we will heuristically use the following simple function which incorporates the stretched exponential function to account for the crossover regime:

$$\frac{W}{A} = C(1 - \exp(-St^{1/2}/C)) + S_g t^{1/2} + S_o \quad (2)$$

where, as before, W is the volume of water absorbed, A is the cross-sectional area of the water exposed surface, and C is a constant which is related to the distance from the concrete surface over which capillary pores control the initial sorption. The coefficient $S_g \ll S$ describes the sorptivity in the smaller pores or the effects of moisture diffusion. We constructed this function so that at early stages, in the limit $t^{1/2} < C/S$, expansion of the exponential gives $C(1 - \exp(-St^{1/2}/C)) \approx St^{1/2}$ which is the same as Equation 1. At long times, the above equation is dominated by the $S_g t^{1/2}$ term.

Figures 4 and 5 show the fitting of data using equation 2. Note the good agreement over four decades in time.

ment over four decades in time. Surprisingly, very good fits were obtained for all the mix designs as well as for different initial saturations. Table 2 contains some representative values of coefficients for equation 2 from fits to our data.

At this point it is appropriate to mention a few caveats. First, Equation 2 cannot describe sorption in its entirety in that the additional $t^{1/2}$ term implies

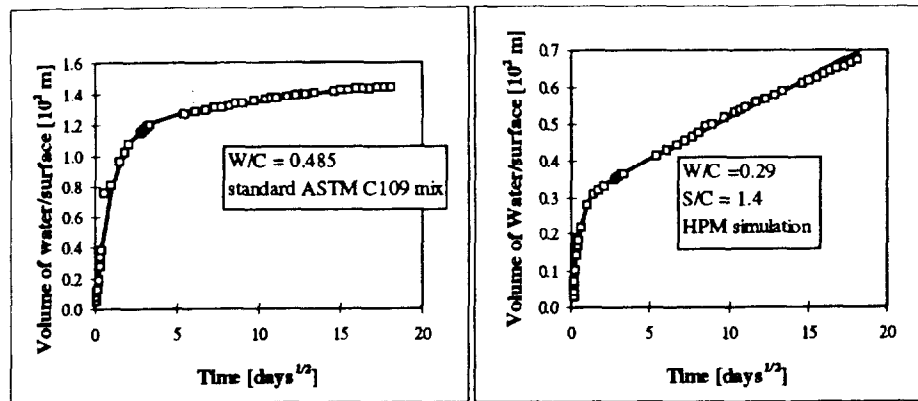


Figure 4: Sorption versus square root of days for mortars. The specimens were oven dried until constant weight, just after demolding (1 day curing).

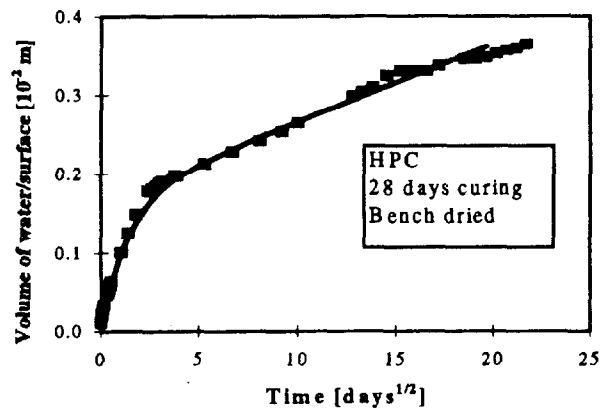


Figure 5: Fit of equation 2 to HPC data.

the specimen would never stop absorbing water. However, given the slowness of the sorption and the fact that capillary rise in small tubes can reach tens of meters, it is possible that Equation 2 may be usable over very long time periods, up to several years. We were unable to accurately determine all the coefficients of equation 2 over very short periods of measurement (of order a few hours) because the power law term will obviously have a greater impact on predicted sorption at later times. If the effect of the smallest pores (or moisture diffusion) is ignored (i.e. setting $S_g = 0$), simple fits of Equation 2, based on data acquired from the first day, give predictions of sorption within 30% of total sorption values recorded over a period of about one year, since the coefficient S_g is small. To closely predict sorption for long periods (i.e. one year) of exposure, we needed data from ten to twenty days of measurements in order to account for the crossover regime. Finally, since the earliest time sorption data was subject

TABLE 2
Parameters from Equation 2 Fit

Specimen	Curing Age [days]	C [10^{-2} m]	S [10^{-2} m/ $\sqrt{\text{days}}$]	S_r [10^{-2} m/ $\sqrt{\text{days}}$]	S_o [10^{-2} m]
ASTM mortar Bench dried	1	0.295	0.4	0.02	0
ASTM mortar Oven dried	1	1.2	1.2	0.015	0
HPM Oven dried	1	0.295	0.65	0.0221	0
Conventional Concrete Bench Dried	28	0.35	0.25	0.009	0
HPC Bench dried	28	0.165	0.12	0.01	0

to the greatest experimental uncertainty we only fit data from the first few hours to about 400 days representing over three orders of magnitude of time.

Appealing aspects of equation 2 include its simplicity and ease of physical interpretation. However, since we did not derive the stretched exponential functional form from basic physical principles, we cannot rule out other "simple" functions that may work as well to describe our data.

Conclusions

A simple scaling form (equation 2) was suggested that accurately fits experimentally measured sorption data for a variety of mortars and concrete which assumes that pores at two different length scales control the sorption. While it is difficult to precisely predict long term trends from measurements taken over very short periods, our data suggests very good estimates, for an exposure period of approximately a year, may be obtained by examining the initial uptake over a period of 10 to 20 days by using equation 2.

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